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Frédérique Battin-Leclerc, A.A. Konnov, J.L. Jaffrezo, Michel Legrand. To better understand the formation of short-chain acids in combustion systems. Combustion Science and Technology, 2008, 180, pp.343-370. 10.1080/00102200701740782 . hal-00206126

**HAL Id: hal-00206126**

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Submitted on 17 Jan 2008

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# **TO BETTER UNDERSTAND THE FORMATION OF SHORT-CHAIN ACIDS IN COMBUSTION SYSTEMS**

F. BATTIN-LECLERC<sup>1\*</sup>, A.A. KONNOV<sup>2</sup>, J.L. JAFFREZO<sup>3</sup> AND M. LEGRAND<sup>3</sup>

<sup>1</sup>Département de Chimie-Physique des Réactions, CNRS-INPL, Nancy, France

<sup>2</sup>Vrije Universiteit Brussel, Brussels, Belgium

<sup>3</sup>Laboratoire de Glaciologie et Géophysique de l'Environnement, CNRS, St Martin d'Hères, France

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\* Corresponding author: DCPR-ENSIC, BP 20541, 1 rue Grandville, BP 20451, 54001 NANCY Cedex, France  
E-mail : Frederique.battin-leclerc@ensic.inpl-nancy.fr ; Tel.: 33 3 83 17 51 25 , Fax : 33 3 83 37 81 20

## Abstract

While their presence at the outlet of IC engines has been attested, the formation of short-chain monocarboxylic acids, formic ( $\text{HCOOH}$ ), acetic ( $\text{CH}_3\text{COOH}$ ), propionic ( $\text{C}_2\text{H}_5\text{COOH}$ ) or acrylic ( $\text{C}_2\text{H}_3\text{COOH}$ ) acids has very rarely been reported in laboratory combustion systems. In order to better understand their potential formation, detailed kinetic mechanisms have been proposed and tested. A first model has been used to simulate lean (equivalence ratios from 0.9 to 0.48) laminar premixed flames of propane stabilized at atmospheric pressure. It was found that amounts up to 40 ppm of formic acid, 25 ppm of acetic acid and 1 ppm of  $\text{C}_3$  acids, mainly acrylic acid, can be formed. A quite acceptable agreement has been obtained with the scarce results from the literature concerning oxygenated compounds, including aldehydes and acids. A reaction pathways analysis demonstrated that each acid is mainly derived from the aldehyde of similar structure, with a dominant role of  $\text{OH}\bullet$  radicals. Based on this first one, a second model has allowed us to simulate a flame of propane doped by toluene and to show, as it was experimentally observed, an enhancement of the formation of  $\text{C}_3$  acid, which could be due to the addition of  $\text{OH}\bullet$  radicals to cyclopentadienone. A third model has been proposed to qualitatively explain the formation of acids during the pre-ignition phase (temperatures below 1100 K) in an HCCI (Homogeneous Charge Compression Ignition) engine alimented by a n-heptane/iso-octane mixture (equivalence ratio of 0.3). Noticeable amounts of monocarboxylic acids could derive from the secondary reactions of ketones or cyclic ethers, which are important products of the oxidation of alkanes at low temperature. These amounts remain too low compared to what is actually observed at the outlet of engines.

**Keywords:** Monocarboxylic acids, laminar flame, HCCI engine, kinetic modeling.

## Introduction

As shown by the review of Chebbi and Carlier (1996), in addition to sulfuric and nitric acids, monocarboxylic acids (formic and acetic acids, especially) can contribute to the acidity of gas and aqueous phases of the atmosphere in urban, as well as in remote regions. Natural and anthropogenic sources of monocarboxylic acids have been proposed, but the nature of the individual sources and their relative importance are not established yet (Legrand et al., 2003). While numerous olefin-ozone reactions can produce formic and acetic acids (Calvert and Stockwell, 1983), it is of importance to better understand the potential direct emissions of monocarboxylic acids from combustion phenomena, from automotive engines especially.

Detailed analyses of gas-phase pollutants emitted from the exhaust have been published for diesel (Zervas et al., 2001a) and gasoline (Zervas et al., 2001b, 2002, 2003) engines. These papers describe the presence of noticeable amounts of monocarboxylic acids. These acids are mainly formic, acetic and propionic acids; the formation of this last one being strongly linked with the presence of aromatic compounds in fuel. In a gasoline engine, the emission of acids corresponds to 4 to 27% of the total amount of emitted hydrocarbons and is larger by a factor of 1.3 to 10 than that of aldehydes; the major compounds being acetic and propionic acids (Zervas et al., 2001b, 2002).

Despite that, acids are very minor oxidation products in most laboratory experimental gas-phase apparatuses and there are very few studies showing their formation during combustion or kinetic model proposed to explain their formation and consumption pathways. Zervas (2005) has analyzed the formation of acids in laminar premixed flames of propane, iso-octane and iso-octane/toluene at atmospheric pressure, for equivalence ratios from 0.8 to 1.2. Curran et al. (2000) have found the presence of formic acid during the oxidation of dimethylether in a flow reactor operated over an initial temperature range of 550–850 K, in the pressure range 12–18 atm, for equivalence ratios from 0.7 to 4.2, and proposed some reaction channels to explain its formation.

The purpose of this paper is first to model<sup>1</sup> the formation of light acids under flame conditions and then to better understand the possible reaction channels which could be responsible for their presence at lower temperature, during the pre-ignition phase in HCCI engines.

### **Modeling of the formation of acids under flame conditions**

The work of Zervas (2005) seems to be the only one showing the presence of light acids under laminar flame conditions; unfortunately, all the data needed for modeling was not provided. By chance, a very detailed study of the temperatures and species profiles in a laminar premixed flame of propane at atmospheric pressure, for equivalence ratios from 0.48 to 0.9, has been recently published by Biet et al. (2005). As the two studies have been performed for some common equivalence ratios, we attempted here to implement a new kinetic mechanism of the formation of acids in a model able to well reproduce the results of Biet et al. (2005) and to use this global model to simulate the relative formation of monocarboxylic acids in the flame of Zervas (2005). Zervas has also observed that the nature of the initial alkane does not much influence the relative formation of acids, but that the presence of toluene increases the formation of C<sub>3</sub> acid. In order to find the chemical reaction responsible for this enhancement, we have added to our first model a submechanism for the oxidation of toluene and run simulations for a propane flame seeded with toluene.

#### *Development of a kinetic model to reproduce the formation of acids in a propane flame*

A mechanism has been written to reproduce the formation and consumption of formic, acetic, propionic and acrylic acids under flame conditions; i.e. the low-temperature reactions of peroxy radicals have not been considered.

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<sup>1</sup> All the models described in this paper are available on request (Frederique.battin-leclerc@ensic.inpl-nancy.fr).

This new mechanism was based on the kinetic scheme (about 800 reactions) of the combustion of propane recently proposed to model laminar premixed flames of methane doped with allene or propyne (Gueniche et al., 2006). This C<sub>3</sub>-C<sub>4</sub> reaction base, which was described in details in a previous paper (Fournet et al., 1999), was built from a review of the recent literature and is an extension of our previous C<sub>0</sub>-C<sub>2</sub> reaction base (Barbé et al., 1995). The C<sub>3</sub>-C<sub>4</sub> reaction base includes reactions involving all the C<sub>3</sub> no-oxygenated species and acrolein, as well as some reactions for selected C<sub>4</sub> and C<sub>5</sub> compounds and the formation of benzene. In this reaction base, pressure-dependent rate constants follow the formalism proposed by Troe (1974) and collisional efficiency coefficients have been included.

To extend this model in order to describe the formation and consumption of acids, the relevant sub-mechanism was adopted from the kinetic scheme proposed by Konnov (2006). The number of species was increased by 31 and the number of new reactions was 197. The formulae and the thermochemical data of the new species are presented in Table I. The complete set of added reactions is given in Table II.

## TABLES I AND II

Thermodynamic data of the following species: HOCO•, HCOO• (formyl radical), HCOOH (formic acid), HCCOH, CH<sub>2</sub>CHOH (vinyl alcohol), CHOCHO, CH<sub>3</sub>CO<sub>2</sub>H (acetic acid) and C<sub>2</sub>H<sub>5</sub>CO• (propionaldehyde radical) were taken from the latest database of Burcat and Ruscic (2006). HiTempThermo database (Allendorf, 2006) was used to obtain the thermochemical data for HCOH• (hydroxymethylene), HOCH<sub>2</sub>O•, HOCH<sub>2</sub>OO•, C<sub>2</sub>H<sub>2</sub>OH• (HOCH=CH•), H<sub>2</sub>CCOH•, •CH<sub>2</sub>CH<sub>2</sub>OOH, •CH<sub>3</sub>CHOOH and other species were Estimated using the software THERGAS (Muller et al., 1995), which is based on the additivity methods proposed by Benson (1976).

Whenever possible, rate constants have been adopted from the literature and reviews, for instance, of Atkinson et al. (1997, 2005); 30 rate constants have been thus found. In many cases, however, rate constants were Estimated assuming same reactivity of similar species. For example, the reactivity of CH<sub>2</sub>(OH)<sub>2</sub>, HOCH<sub>2</sub>OO•, HOCH<sub>2</sub>OOH and H<sub>2</sub>CCOH• were assumed analogous to

$\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{O}_2$ ,  $\text{CH}_3\text{O}_2\text{H}$  and  $\text{C}_2\text{H}_2\text{OH}\cdot$ , respectively. Strictly speaking this approach could be more or less valid for true homologues; remote similarity could be misleading due to resonance stabilization of radicals, significant modifications of the bond dissociation energy, etc. On the other hand, this is probably the only way for exploratory modelling of the formation of acids, which are usually not included in the contemporary combustion mechanisms.

A few modifications of the sub-mechanism adopted from the Konnov (2006) kinetic scheme were made. The rate constant of reaction (12) of addition of  $\text{OH}\cdot$  radicals to formaldehyde is taken as 0.3% that of the H-abstraction, which is in agreement with the value of 4% proposed by Sivakumaran et al. (2003) as an upper limit for this branching ratio at 298 K. This experimental study of the reaction between  $\text{OH}\cdot$  radicals with formaldehyde by laser photolysis led Sivakumaran et al. (2003) to think that the rate constant of the addition was very small as no hydrogen atoms could be observed by resonance fluorescence. As discussed by Taylor et al. (2006), the addition of  $\text{OH}\cdot$  radicals to acetaldehyde giving methyl radicals and formic acid or H-atoms and acetic acid could have been envisaged, but has been shown to be negligible compared to the two possible H-abstractions. The rate constant of the combinations between  $\text{OH}\cdot$  and carbonyl radicals was taken as that proposed by Allara et al. (1980) for H-atoms. The reactions of propionic and acrylic acids have been deduced from those proposed for acetic acid.

#### Validation of the model by modeling the evolution of the main species in a propane flame

All the simulations have been performed using PREMIX code of the CHEMKIN II collection (Kee et al., 1993) with Estimated transport coefficients and temperature profiles taken from the experiments. Comparisons between experimental results of Biet et al. (2005) and simulations of a laminar premixed propane flame are shown in fig. 1 for  $\phi = 0.9$  and in fig. 2 for  $\phi = 0.48$ .

#### **FIGURES 1 AND 2**

As it can be seen in fig. 1a and 2a, a correct agreement is obtained for the consumption of propane and oxygen and the formation of carbon dioxide for both equivalence ratios. Figure 1b and 1c show that the formation of water, hydrogen, carbon monoxide and C<sub>2</sub> compounds are also well reproduced by the model at  $\phi = 0.9$ . Similarly good agreement is obtained for  $\phi = 0.48$ , as it can be seen in fig. 2b and 2c. Figures 1d and 2d display the profiles of aldehydes showing that the modelling of formaldehyde and acetaldehyde is also acceptable. These figures also present our prediction for propionaldehyde and acrolein, which are in agreement with the limit of detection of 100 ppm given by Biet et al. (2005).

It is worth noting that the decrease in equivalence ratio does not change markedly the formation of carbon monoxide and aldehydes. That was well explained by Biet et al. (2005) by defining an “effective equivalence ratio” based on the proportion of oxygen consumed in the flame and showing that it was always close to 1 when oxygen was in excess.



### Simulation of the formation of short-chain carboxylic acids in a propane flame

Figure 3 presents the simulated profiles of acids obtained under the same conditions as the flame of Biet et al. (2005) using the mechanism above described. This figure shows that small amounts of acids are actually produced in this flame, the major ones being formic and acetic acids. Amongst C<sub>3</sub> acids, the main one is acrylic acid. That is directly related to the activation energy for the beta-scission involving the breaking of the C-CO bond for CH<sub>2</sub>=CH-CO• radicals (E<sub>a</sub> = 34.0 kcal/mol (Marinov et al., 1996), ΔH<sub>r</sub> (298K) = 26.2 kcal/mol) and for CH<sub>3</sub>-CH<sub>2</sub>-CO• radicals (E<sub>a</sub> = 14.4 kcal/mol (reaction 174 in Table II), ΔH<sub>r</sub> (298K) = 11.9 kcal/mol); everywhere in the text, carbonyl radicals (R-C•(=O)) are noted RCO•. The unsaturated oxygenated radical is less easily decomposed than the saturated one to give carbon monoxide (by a factor 6x10<sup>-3</sup> at 1400 K), its concentration is then larger, which favours its combination with OH• radicals.

### **FIGURE 3**

Figure 3 also shows that the formation of acids in these lean flames does not change much when decreasing the equivalence ratio; only the maximum mole fractions of formic and acrylic acids are slightly increased. That is in agreement with what was noticed by Biet et al. (2005) for the formation of aldehydes, but in disagreement with the experimental results of Zervas (2005) showing an increase of about a factor 2 of the formation of formic and acetic acids when varying the equivalence ratio from 1.17 to 0.77.

Figure 4 displays a comparison between the computed proportions (the ratio between the mole fraction of each acid and the sum of their mole fractions) of acids and the experimental ones measured by Zervas et al. (2005) for an equivalence ratio of 0.9. In Zervas's work, organic acids were collected in deionised water and analysed by two methods: ionic chromatography/conductimetry detection for formic acid and gas chromatography/flame ionisation detection for other acids. Details about the collection, the analysis and the calibration can be found in a previous paper of Zervas et al. (1999). The analysis by gas chromatography/flame ionisation detection has been tested for nine aliphatic acids from C<sub>2</sub> to C<sub>7</sub>, but not for acrylic acid. It is

therefore difficult to know if the two  $C_3$  acids could have been separated under these conditions. Figure 4 shows that, apart from the disagreement concerning the nature of the  $C_3$  acid, the proportion between  $C_1$ ,  $C_2$  and  $C_3$  acids is well captured by the model.

#### FIGURE 4

Figure 5 presents the main pathways of formation of the four monocarboxylic acids studied for an equivalence ratio of 0.9. It can be seen that these acids are mainly derived from the aldehyde having the same structure.

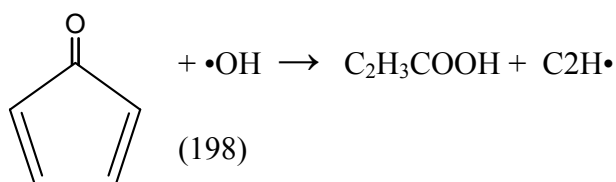
- Formic acid is 99% obtained from the addition of  $OH\bullet$  radicals to formaldehyde, followed by the elimination of a hydrogen atom.
- Acetic acid is mainly formed from the combination of  $OH\bullet$  and  $CH_3CO\bullet$  radicals. These last radicals are produced for 40% from reactions of acetaldehyde (directly by abstraction of the carboxylic H-atom or via the formation of  $\bullet CH_2CHO$  radicals followed by a beta-scission and the addition of H-atoms to ketene,  $CH_2=C=O$ ), but also for 40% from propene and for 20% from vinyl radicals, which are mainly obtained from reactions of ethylene. Propene and vinyl radical can react with O-atoms to give ketene. The reactions of ketene with H-atoms leading to  $CH_3CO\bullet$  radicals are responsible for 70% of the formation of these radicals.
- Propionic acid is derived from  $C_2H_5CO\bullet$  radicals by combination with  $OH\bullet$  radicals.  $C_2H_5CO\bullet$  radicals are produced for 60% from propionaldehyde by H-abstraction by small radicals and for 40% from reactions between methyl radicals and ketene.
- Acrylic acid is only produced from acrolein by H-abstraction by small radicals, followed by a combination of the obtained carbonyl ( $C_2H_3CO\bullet$ ) radicals with  $OH\bullet$  radicals.

**FIGURE 5**

*Simulation of the formation of short-chain carboxylic acids in a propane flame doped by toluene*

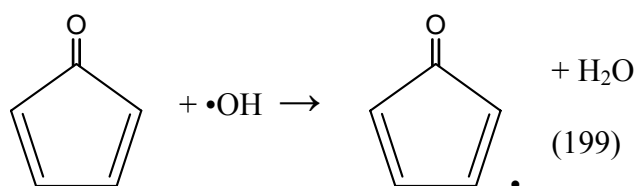
The sub-mechanisms (about 360 reactions) for the oxidation of benzene and toluene developed by Da Costa et al. (2003) and Bounaceur et al. (2005), respectively, have been added to the above described model. As we are not aware of experimental results which could have been of help for validation, simulations have been run under the same conditions as for the flame of propane of Biet et al. (2005) at  $\phi=0.9$ , but with an addition of 10% toluene (relative to the mole fraction of propane). The computed proportions of acids are mostly unchanged, the amounts of each compound being slightly lower, i.e. the maximum mole fraction is 30 ppm for formic acid, 18 ppm for acetic acid and 0.2 ppm for acrylic acid. This decrease is due to a lower concentration of  $\text{OH}\cdot$  radicals in the flame in presence of toluene, which easily leads to the formation of resonance stabilised benzyl radicals.

Figure 6 presents the computed profiles of the main formed aromatic species, toluene, benzene, cyclopentadiene, phenol, benzaldehyde, cyclopentadienone, ethylbenzene, styrene, cresols and benzoquinone. Several secondary reactions of these compounds leading to  $\text{CH}_2=\text{CH}-\text{CO}\cdot$  radicals have been tested, but the only channel leading to a strong increase in the formation of  $\text{C}_3$  acids was the following addition of  $\text{OH}\cdot$  radicals to cyclopentadienone (198):



with an A-factor of  $2 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and an activation energy of -1 kcal/mol, which are usual rate parameters for an addition to a double bond. This reaction involves the opening of the cycle and a rearrangement involving a H-transfer. The reaction between  $\text{OH}\cdot$  and cyclopentadienone has never

been experimentally investigated. During their study of the oxidation of benzene, Alzueta et al. (2000) have written the abstraction of H-atoms (199):



which is also considered in our mechanism. The addition of OH• radicals to acetone leading to the formation of acetic acid and methyl radicals has been proposed as a very minor channel of the reaction between OH• radicals and acetone. Talukdar et al. (2003), Vandenberg et al. (2002) and Tyndall et al. (2002) have reported an upper limit of 1%, 5% and 10 %, respectively. The addition of OH• radicals to other linear ketones (propanone, butanone, pentanone) has been found negligible by Tranter and Walker (2001), as the formation of acids was not observed.

**FIGURE 6**

Figure 7 presents the simulated profiles of acids obtained with a mechanism including reaction (198) under the same conditions as the flame of propane of Biet et al. (2005) at  $\phi=0.9$ , but with an addition of 10% toluene (relative to the mole fraction of propane), and shows an important increase of the formation of acrylic acid. The maximum mole fraction of this C<sub>3</sub> acid is thus multiplied by a factor above ten by the addition of toluene and is now the major acid in the flame. In the iso-octane/toluene flame studied by Zervas (2005), the C<sub>3</sub> acid is also the major one, but is identified as propionic acid.

**FIGURE 7**

### **Modeling of the formation of acids during the pre-ignition phase in an HCCI engines**

As shown in the previous sections, under flame conditions, the predicted amounts of acids are about forty times lower than that of aldehydes, explaining why the formation of acids is usually not reported in flame experiments. If the emissions of acids from engines are really larger than those of aldehydes, as reported by Zervas et al. (2001b) at the exhaust of gasoline engines, low

temperature reactions should be of particular importance to explain this observation. In order to better understand these reactions, simulations have been run under the HCCI conditions used by Dubreuil et al. (2007) using the SENKIN code (Kee et al., 1993) to compute the evolution of a 25% n-heptane/75% iso-octane mixture in air ( $C_7H_{16}$  : 0,413% ;  $C_8H_{18}$  : 0,1377% ;  $O_2$  : 20,9% ;  $N_2$  : 78,55%,  $\phi = 0.3$  ) in a variable volume, zero-dimensional adiabatic single zone reactor. The kinetic model (around 7800 reactions) has been automatically generated by the EXGAS software for the oxidation of a n-heptane/iso-octane/1-heptene mixture. The rules of generation have been described by Warth et al. (1998) and Buda et al. (2005) for alkanes and by Touchard et al. (2005) for alkenes. Low-temperature reactions have been considered, including all the reactions of peroxy, hydroperoxy and peroxyhydroperoxy radicals. The need to consider a comprehensive model for the oxidation of 1-heptene, a secondary product of n-heptane, will be seen further in the text.

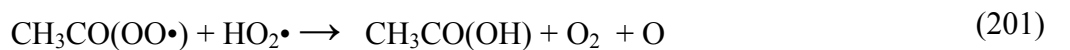
Single-zone modelling allows a satisfactory prediction of ignition delay times as shown by Dubreuil et al. (2007), but not at all a good modelling of the composition of exhaust gases, the final products under lean conditions being only carbon dioxide and water. Even the formation of carbon monoxide is underpredicted by a factor  $10^5$ . However, assuming that the temperature gradients in the combustion chamber are weak when the temperature rise is still slow (see fig. 8), these computations could give some clues about the species evolution during the pre-ignition phase, as displayed in fig. 8 for the main  $C_1$ - $C_3$  and  $C_7$ - $C_8$  oxygenated species. This figure shows that the evolution of the mole fraction of each of these species presents a “plateau” during the pre-ignition zone, i.e. for residence times between  $17.5 \times 10^{-3}$  and  $18.5 \times 10^{-3}$  s. Assuming that the presence of oxygenated organic species in the exhaust gases is due to the existence of cold zones of the combustion chamber (e. g. near the walls or in crevices) (Aceves et al., 2004), in which the ignition does not reach its final stage, their repartition is probably close to what is observed during this “plateau”. While the combustion phenomena are different in HCCI and spark-ignited engines (homogeneous auto-ignition in the first one and premixed flame propagation in the second one), the chemistry occurring in the cold zones is probably similar in both systems. Figure 9 shows that the

mole fractions of acetaldehyde, acrolein, propionaldehyde and methanol relative to that of formaldehyde and obtained by our simulation under the conditions of fig. 8 at a residence time of  $18.5 \times 10^{-3}$  s are in good agreement with those measured by Zervas et al. (2002) in a gasoline engine alimanted by a fuel rich in iso-octane at an equivalence ratio of 1. This agreement, which is unexpectedly satisfactory according to the roughness of the hypotheses made, the difference of equivalence ratios and the possibility of reaction in the exhaust line, led us to think that our simulation was not unreasonable and that it could be used to investigate the ways of formation of acids in engines.

### FIGURES 8-9

Figure 10 presents the evolution obtained for the different C<sub>1</sub>-C<sub>3</sub> acids and formaldehyde using the five following models:

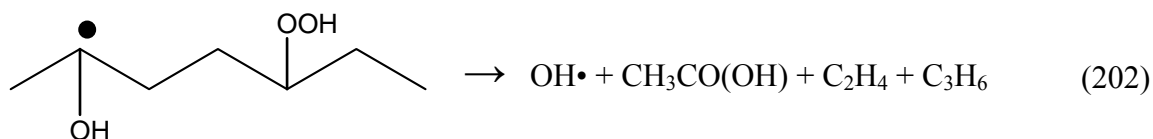
- Model 1 is obtained by just adding the sub-mechanism for the formation and consumption of acids previously described for flames simulation to the model of the low-temperature oxidation of a n-heptane/iso-octane/1-heptene mixture. The formation of acids is very small and occurs mainly during the autoignition, when the concentration of OH• radicals is large enough; the main compound is formic acid, but its concentration in the pre-ignition zone (at a residence time of  $18.5 \times 10^{-3}$  s) is about 1500 times less than that of formaldehyde. The concentrations of acetic and propionic acids are still  $10^5$  times lower than that of formic acid.
- Model 2 also contains additional reactions for CH<sub>3</sub>CO(OO•) radicals, which are obtained by addition to oxygen molecules of CH<sub>3</sub>CO• radicals, which derive from acetaldehyde. The reactions (200) and (201) proposed by Tomas et al. (2001) have been included:



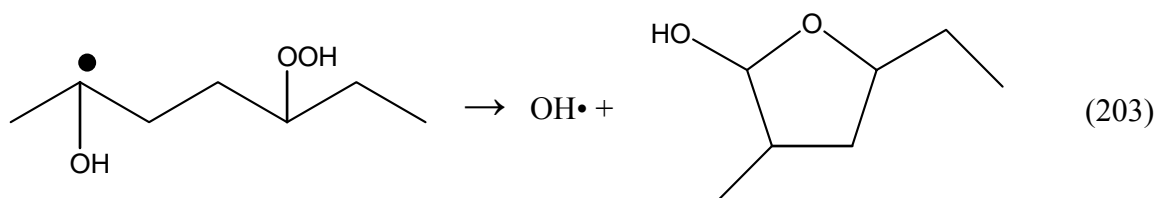
with an A-factor of  $3.8 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for reaction (200) and of  $7.7 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for reaction (201) and an activation energy of  $-1.8 \text{ kcal/mol}$  for both reactions, as determined by

these authors. As reaction (200) involves a formation of acid from a radical deriving from acetaldehyde, it was found promising. The addition of these reactions has an effect on the production of acetic acid in the pre-ignition zone, but, while the concentration of this acid has been multiplied by a factor almost 100 at a residence time of  $18.5 \times 10^{-3}$  s, this effect is not strong enough. Around 1000 K, the temperature during the preignition zone, the decomposition of  $\text{CH}_3\text{CO}\cdot$  radicals is about 1000 times faster than the addition to oxygen molecules.

- Model 3 includes the decomposition (202) of the hydroxyhydroperoxy radicals, which are obtained from 1-heptene, a secondary product of the oxidation of n-heptane, by addition of  $\text{OH}\cdot$  radicals, followed by an addition to oxygen molecules and isomerizations:

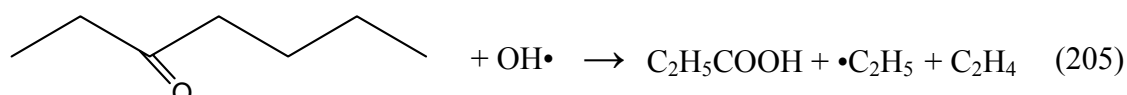
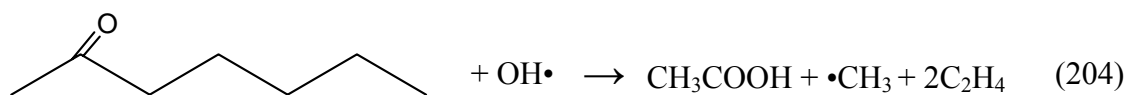


The globalized reaction (202) is written instead of reaction (203), which involves the formation of a hydroxy cyclic ether, a species never experimentally observed during the oxidation of alkenes (Touchard et al., 2005):



Considering that both exothermic reactions occur through the same transition state, the same rate parameters have been assumed, an A-factor of  $3.6 \times 10^9 \text{ s}^{-1}$  and an activation energy of 7 kcal/mol, as proposed by Touchard et al. (2005). The addition of this reaction has a clear influence on the production of acetic acid in the pre-ignition zone, its concentration compared to model 2 being multiplied by a factor almost 50 at a residence time of  $18.5 \times 10^{-3}$  s. Nevertheless, while we have chosen the reaction of this type with the largest flow rate, as the formation of five-membered rings is favored as discussed further in the text, the concentration of acetic acid is still 100 and 10000 times lower than those of formic acid and formaldehyde, respectively.

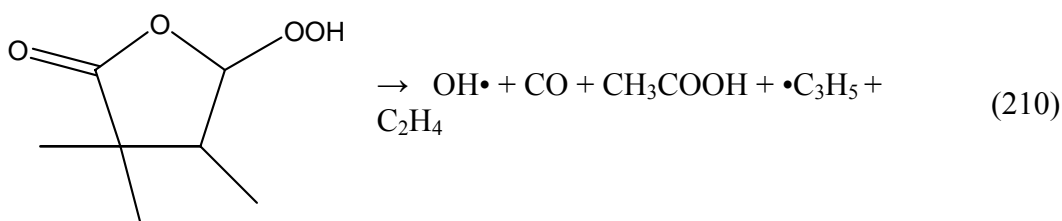
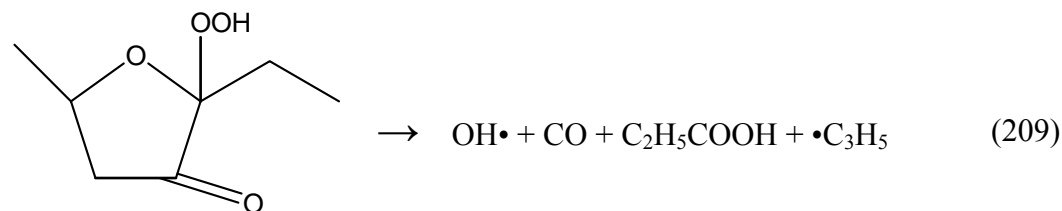
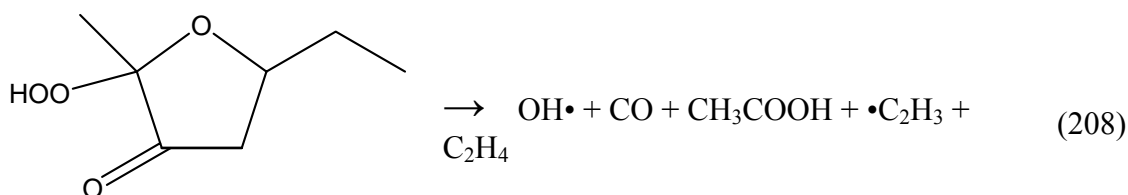
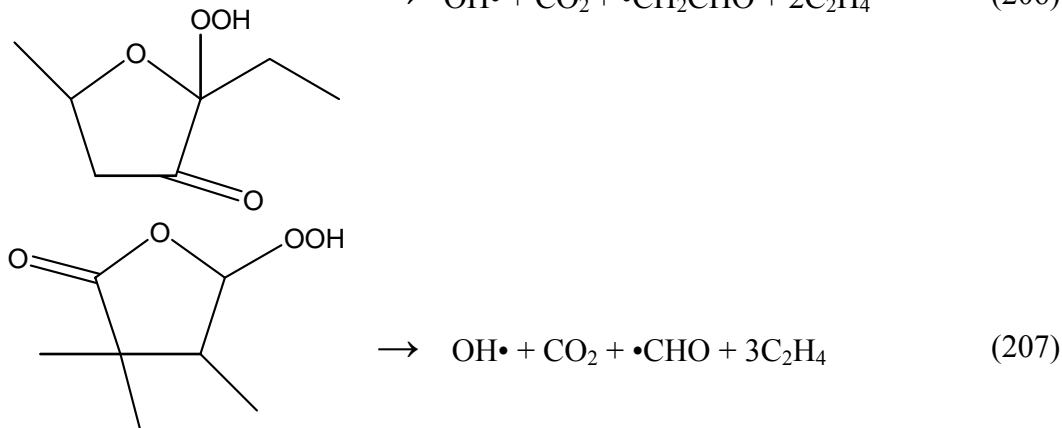
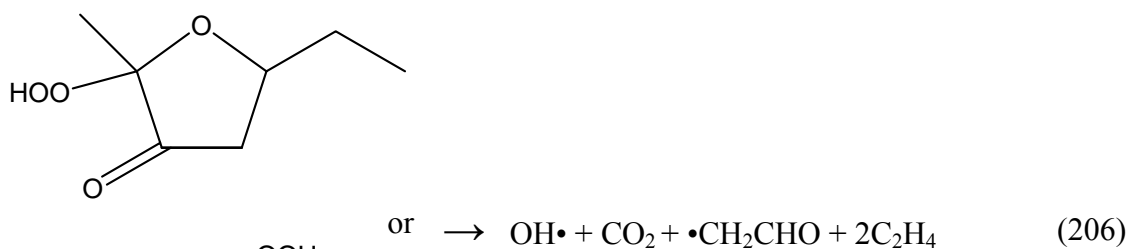
- Despite that the addition of OH• radicals to linear C<sub>3</sub>-C<sub>5</sub> ketones has been found negligible under the conditions used by Tranter and Walker (2001), model 4 has been made in order to test the potential influence of the additions (204) and (205) of OH radicals to 2- and 3-heptanones, which are important primary products of the oxidation of n-heptane, as shown in fig. 8b:



with rate parameters deriving from those proposed for reaction (198). In order to have a manageable size, the secondary mechanisms generated by the EXGAS software (Warth et al., 1998) involves lumped reactants (the molecules formed in the primary mechanism, with the same molecular formula and the same functional groups, are lumped into one unique species, without distinguishing between the different isomers) and includes global reactions. The different isomers of heptanone are then not distinguished, but both reactions (204) and (205) are considered, with rate constants reflecting the ratio between the flow rates of formation of 2- and 3-heptanones. The inclusion of these reactions has a spectacular effect on the production of acetic and propionic acids, which are now the major acids obtained, but with a concentration still about 400 times less than that of formaldehyde at a residence time of  $18.5 \times 10^{-3}$  s.

- In model 5, the decompositions of the ketohydroperoxides obtained by secondary reactions of cyclic ethers obtained in the oxidation of n-heptane (206) and iso-octane (207) have been replaced by the decompositions (208), (209) and (210), respectively:





The decomposition of ketohydroperoxide deriving from dimethyl ether has been proposed by Curran et al. (2000) to explain the formation of formic acid. The used rate parameters are an A-factor of  $7.5 \times 10^{15} \text{ s}^{-1}$ , for reactions (208) and (209), and of  $1.5 \times 10^{16} \text{ s}^{-1}$  for reaction (210) and an activation energy of 42 kcal/mol, as proposed by Buda et al. (2005). Cyclic ethers react first by an H-abstraction and, as proposed by Glaude et al. (2000), the radicals obtained from cyclic ethers including more than 3 atoms can also react with oxygen. These reactions with oxygen

involves the classical sequence of oxygen addition, isomerization, second oxygen addition, second isomerization and beta-scission to lead to the formation of ketohydroperoxydes, degenerate branching agents, which decomposes by reactions such as decompositions (206) and (207). As shown in fig. 8b, for a given alkane, the main produced cyclic ethers are five-membered rings (furans); the formation of four-membered (oxirans) and six-membered (pyrans) rings being less important. It is why we have tested the potential formation of acids only for the decompositions of the ketohydroperoxydes deriving from five-membered cyclic ethers. The changes in these reactions leads again to an important increase of the formation of acids, but the concentration of formadehyde still keeps a value about 80 times larger than that of acetic acid, the major acid obtained, at a residence time of  $18.5 \times 10^{-3}$  s.

### FIGURE 10

The addition of  $\text{OH}\cdot$  radicals to long chain ketones and the decomposition of the ketohydroperoxydes deriving from cyclic ethers seem to be the two most interesting ways to explain the presence of acids in exhaust gases. While the flow rate of formation of heptanones is larger than that of cyclic ethers, the production of acids is larger through this second type of compound, because ketones react mainly by H-abstraction under the studied conditions. While ways of formation of acids have been envisaged from the major oxygenated products of the oxidation of n-heptane and iso-octane, none of the tested models allows us to predict a higher formation of acids compared to formaldehyde. This could be due to a reaction channel which has not been envisaged and to the uncertainties linked with the single-zone modelling, but one could also consider the possibility of reactions in the exhaust line, may be also of heterogeneous reactions with the metallic parts.

### Conclusion

A new model has been proposed to simulate the formation of monocarboxylic acids from  $\text{C}_1$  to  $\text{C}_3$  in laminar premixed flames of propane. This model has allowed us to correctly reproduce the proportions between  $\text{C}_1$ ,  $\text{C}_2$  and  $\text{C}_3$  acids experimentally measured. Under these conditions,  $\text{C}_1$ - $\text{C}_3$

acids are mainly derived from the aldehyde having the same structure, by addition of OH• radicals for formic acid and by combination of carbonyl and OH• radicals for heavier acids. The addition of OH• radicals to cyclopentadienone is a possible way to explain an enhancement of the amount of C<sub>3</sub> acid when toluene is added to the flame.

Under the conditions of the pre-ignition zone of an HCCI engine, the addition of OH• radicals to long chain ketones and the decomposition of the ketohydroperoxydes deriving from cyclic ethers could account for the formation of acetic and propionic acids as the major acids, but the obtained amounts are much lower than that of formaldehyde. These reactions should be considered as first tracks, which need to be more thoroughly investigated by means of additional experimental and theoretical work. A better understanding of the way of formation of monocarboxylic acids in the combustion chamber, but also in the exhaust line, would help to know whether internal combustion engines are really an important primary source of atmospheric emissions of these compounds.

## Acknowledgements

C. Mounaïm-Rousselle and A. Dubreuil from the LME in Orléans are gratefully thanked for providing data for the simulations in an HCCI engine.

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**TABLE I: NAMES, FORMULAE AND HEATS OF FORMATION (298K), ENTROPY (298K) AND SPECIFIC HEAT (300K) FOR SPECIES INVOLVED IN TABLE II, WHICH WERE NOT CONSIDERED BY GUENICHE ET AL. (2006).**

Thermochemical data are given in cal, mol, K units.

Name	Formula	$\Delta H_f / 1000$	S	$C_p$	Name	Formula	$\Delta H_f / 1000$	S	$C_p$
<b>C<sub>1</sub> species</b>									
HCOOH	H-C(=O)-OH	-90.5	59.1	9.9	HCOH <sup>a</sup>	H-C(-OH) ••	49.5	57.2	10.5
HOCO	HO-C(=O) •	-43.3	60.2	10.4	HCOO	H-C(=O)-O•	-36.0	57.3	9.6
HOCHOH	HO-CH(-OH) •	-48.1	66.7	11.0	HOCH <sub>2</sub> O	HO-CH <sub>2</sub> -O•	-39.1	63.2	12.5
CH <sub>2</sub> (OH) <sub>2</sub>	HO-CH <sub>2</sub> -OH	-91.0	64.5	11.3	HOCH <sub>2</sub> OO	HO-CH <sub>2</sub> -O-O•	-37.1	69.1	16.0
HOCH <sub>2</sub> OOH	HO-CH <sub>2</sub> -O-OH	-75.2	74.1	15.9					
<b>C<sub>2</sub> species</b>									
CH <sub>3</sub> CO <sub>2</sub> H	CH <sub>3</sub> -C(=O)-OH	-103.0	67.7	15.2	HCCOH	H-C≡C-OH	22.3	59.5	13.8
C <sub>2</sub> H <sub>2</sub> OH	H-C(•)=C-OH	30.3	62.4	13.9	H <sub>2</sub> CCOH	H <sub>2</sub> C=C (-OH)•	28.2	64.2	13.3
CH <sub>2</sub> CHOH	H <sub>2</sub> C=C-H(-OH)	-29.8	69.3	14.6	CHOCO	O=CH-C=O	-13.8	39.1	11.6
CHOCHO	O=CH-CH=O	-50.7	65.1	14.3	HOCH <sub>2</sub> CO	HO-CH <sub>2</sub> -C(=O)•	-39.5	75.6	16.0
HOCH <sub>2</sub> CHO	HO-CH <sub>2</sub> -C-H(=O)	-74.8	74.1	17.0	HOCHCHO	HO-CH(•)-CH=O	-32.5	72.1	16.7
CHCHOOH	HC(•)=CH-O-OH	51.6	74.1	18.2	CH <sub>3</sub> CO <sub>2</sub>	CH <sub>3</sub> -C(=O)-O•	-50.3	65.6	14.0
C <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	CH <sub>2</sub> =CH(-O-O•)	27.9	68.5	17.1	C <sub>2</sub> H <sub>3</sub> OOH	CH <sub>2</sub> =CH(-O-OH)	-72.5	73.0	18.8
CH <sub>3</sub> CHOOH	CH <sub>3</sub> -CH(•)-O-OH	74.5	74.5	20.2					
<b>C<sub>3</sub> species</b>									
C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H	CH <sub>3</sub> -CH <sub>2</sub> -C(=O)-OH	-106.0	76.9	21.9	C <sub>2</sub> H <sub>3</sub> CO <sub>2</sub> H	CH <sub>2</sub> =CH-C(=O)-OH	-80.4	75.2	18.7
C <sub>2</sub> H <sub>5</sub> CO	CH <sub>3</sub> -CH <sub>2</sub> -C(=O) •	-86.1	73.1	18.3	C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub>	CH <sub>3</sub> -CH <sub>2</sub> -C(=O)-O•	-52.0	75.0	19.9
C <sub>2</sub> H <sub>5</sub> COOO	CH <sub>3</sub> -CH <sub>2</sub> -C(=O)-O-O•	-51.4	85.6	21.8	C <sub>2</sub> H <sub>5</sub> COOOH	CH <sub>3</sub> -CH <sub>2</sub> -C(=O)-O-O-H	-86.5	90.1	23.5
C <sub>2</sub> H <sub>3</sub> CO <sub>2</sub>	CH <sub>2</sub> =CH-C(=O)-O•	-26.4	73.3	16.7					

<sup>a</sup> : Triplet state.

**TABLE II: COMPLETE LIST OF THE REACTIONS CONCERNING C<sub>1</sub>, C<sub>2</sub> AND C<sub>3</sub> OXYGENATED COMPOUNDS WHICH WERE NOT PART OF THE MECHANISM FOR THE OXIDATION OF ALLENE AND PROPYNE PROPOSED BY GUENICHE ET AL. (2006). THESE REACTIONS WERE MAINLY PROPOSED BY KONNOV (2006).**

**The rate constants are given ( $k=A T^n \exp(-E_a/RT)$ ) in cc, mol, s, cal units.**

No	Reaction	A	n	E <sub>a</sub>	Reference
<b>C<sub>1</sub> species</b>					
1	CH <sub>3</sub> +OH=HCOH+H <sub>2</sub>	2.28E+10	-0.12	-415	Baulch et al., 2005
2	HCOH+OH=CO <sub>2</sub> +H <sub>2</sub> +H	1.08E+13	0	0	Humpfer et al., 1995
3	HCOH+HCHO=HOCH <sub>2</sub> CHO	1.00E+11	0	0	Estimate
4	HCOH+CH <sub>3</sub> =CH <sub>2</sub> CHOH+H	7.00E+13	0	0	Estimate
5	C <sub>2</sub> H <sub>4</sub> +HCOH=C <sub>2</sub> H <sub>6</sub> +CO	1.00E+11	0	0	Estimate
6	CO+OH(+M)=HOCO(+M)	1.20E+07	1.83	-236	Senosiain et al., (2003)
	LOW	7.20E+25	-3.85	1550	
	TROE /0.6 10. 100000./				
7	HOCO(+M)=H+CO <sub>2</sub> (+M)	1.74E+12	0.307	32930	Larson et al., 1988
	LOW	2.29E+26	-3.02	35070	
8	HOCO+O <sub>2</sub> =HO <sub>2</sub> +CO <sub>2</sub>	1.26E+12	0	0	Petty et al., 1993
9	CH <sub>3</sub> CO+OH=CH <sub>3</sub> +HOCO	3.00E+13	0	0	Tsang and Hampson, 1986
10	HCOO+M=H+CO <sub>2</sub> +M	8.70E+15	0	14400	Same rate constant as for the decomposition of CH <sub>3</sub> CO <sub>2</sub>
11	HCOO+O <sub>2</sub> =CO <sub>2</sub> +HO <sub>2</sub>	1.00E+11	0	0	Estimate
12	HCOOH+M=CO+H <sub>2</sub> O+M	2.10E+14	0	40400	Saito et al., 1984
13	HCOOH+M=CO <sub>2</sub> +H <sub>2</sub> +M	1.50E+16	0	57000	Hsu et al., 1982
14	HCOOH+OH=HOCO+H <sub>2</sub> O	1.00E+11	0	0	Estimate
15	HCOOH+OH=HCOO+H <sub>2</sub> O	1.00E+11	0	0	Estimate
16	HCOOH+HCOO=HOCO+HCOOH	1.00E+11	0	0	Estimate
17	HCHO+OH=HOCH <sub>2</sub> O	3.40E+06	1.18	-400	See present work
18	HOCH <sub>2</sub> O=HCOOH+H	1.00E+14	0	14900	Estimate
19	HOCH <sub>2</sub> O+O <sub>2</sub> =HO <sub>2</sub> +HCOOH	2.10E+10	0	0	Estimate
20	HOCH <sub>2</sub> O+HCHO=CH <sub>2</sub> (OH) <sub>2</sub> +CHO	6.00E+08	0	0	Estimate
21	CH <sub>2</sub> (OH) <sub>2</sub> (+M)=CH <sub>2</sub> OH+OH(+M)	1.70E+16	0	90885	Same reactivity
	LOW	6.60E+16	0	65730	assumed as CH <sub>3</sub> OH (Konnov, 2000)
	TROE /0.82 200.0 1438.0/				
22	CH <sub>2</sub> (OH) <sub>2</sub> (+M)=HOCHOH+H(+M)	1.38E+16	0	95950	Same reactivity
	LOW	5.35E+16	0	70800	assumed as CH <sub>3</sub> OH
	TROE /0.82 200.0 1438.0/				
23	CH <sub>2</sub> (OH) <sub>2</sub> +H=HOCHOH+H <sub>2</sub>	1.64E+07	2.0	4520	Same reactivity assumed as CH <sub>3</sub> OH
24	CH <sub>2</sub> (OH) <sub>2</sub> +H=H <sub>2</sub> +HOCH <sub>2</sub> O	4.00E+13	0	6095	Same reactivity assumed as CH <sub>3</sub> OH
25	CH <sub>2</sub> (OH) <sub>2</sub> +O=HOCHOH+OH	1.63E+13	0	5030	Same reactivity assumed as CH <sub>3</sub> OH
26	CH <sub>2</sub> (OH) <sub>2</sub> +O=HOCH <sub>2</sub> O+OH	1.00E+13	0	4680	Same reactivity assumed as CH <sub>3</sub> OH
27	CH <sub>2</sub> (OH) <sub>2</sub> +OH=HOCHOH+H <sub>2</sub> O	1.44E+06	2.0	-840	Same reactivity assumed as CH <sub>3</sub> OH
28	CH <sub>2</sub> (OH) <sub>2</sub> +OH=HOCH <sub>2</sub> O+H <sub>2</sub> O	1.00E+13	0	1700	Same reactivity assumed as CH <sub>3</sub> OH
29	CH <sub>2</sub> (OH) <sub>2</sub> +O <sub>2</sub> =HOCHOH+HO <sub>2</sub>	2.05E+13	0	44900	Same reactivity assumed as CH <sub>3</sub> OH
30	CH <sub>2</sub> (OH) <sub>2</sub> +HO <sub>2</sub> =HOCHOH+H <sub>2</sub> O <sub>2</sub>	9.64E+10	0	12580	Same reactivity assumed as CH <sub>3</sub> OH
31	CH <sub>2</sub> (OH) <sub>2</sub> +B <sub>5</sub> CH <sub>2</sub> =CH <sub>3</sub> +HOCHOH	3.19E+01	3.2	7200	Same reactivity assumed as CH <sub>3</sub> OH
32	CH <sub>2</sub> (OH) <sub>2</sub> +B <sub>5</sub> CH <sub>2</sub> =CH <sub>3</sub> +HOCH <sub>2</sub> O	1.44E+01	3.1	6900	Same reactivity assumed as CH <sub>3</sub> OH
33	CH <sub>2</sub> (OH) <sub>2</sub> +CH <sub>3</sub> =HOCHOH+CH <sub>4</sub>	3.19E+01	3.17	7172	Same reactivity assumed as CH <sub>3</sub> OH

34	$\text{CH}_2(\text{OH})_2 + \text{CH}_3 = \text{HOCH}_2\text{O} + \text{CH}_4$	$1.45\text{E}+01$	3.1	6935	Same reactivity assumed as $\text{CH}_3\text{OH}$
35	$\text{HCHO} + \text{HO}_2 = \text{HOCH}_2\text{OO}$	$5.80\text{E}+09$	0	-1242	Atkinson et al., 1997
36	$\text{CH}_2\text{OH} + \text{O}_2 = \text{HOCH}_2\text{OO}$	$1.50\text{E}+14$	-1.0	0	Rate constant taken as 10% as that used by Konnov (2000) for the channel leading to $\text{HCHO}$ at low temperature
37	$\text{HOCH}_2\text{OO} + \text{HO}_2 = \text{HCOOH} + \text{H}_2\text{O} + \text{O}_2$	$3.37\text{E}+09$	0	-4570	Atkinson et al. 1997
38	$\text{HOCH}_2\text{OO} + \text{HOCH}_2\text{OO} = \text{HCOOH} + \text{CH}_2(\text{OH})_2 + \text{O}_2$	$3.40\text{E}+10$	0	-1490	Wallington et al. 1992
39	$\text{HOCH}_2\text{OO} + \text{HOCH}_2\text{OO} = \text{HOCH}_2\text{O} + \text{HOCH}_2\text{O} + \text{O}_2$	$3.31\text{E}+12$	0	0	Burrows et al. 1989
40	$\text{HOCH}_2\text{OO} + \text{H} = \text{HOCH}_2\text{O} + \text{OH}$	$9.60\text{E}+13$	0	0	Same reactivity assumed as $\text{CH}_3\text{O}_2$ (Konnov, 2000)
41	$\text{HOCH}_2\text{OO} + \text{O} = \text{HOCH}_2\text{O} + \text{O}_2$	$3.60\text{E}+13$	0	0	Same reactivity assumed as $\text{CH}_3\text{O}_2$
42	$\text{HOCH}_2\text{OO} + \text{OH} = \text{CH}_2(\text{OH})_2 + \text{O}_2$	$6.00\text{E}+13$	0	0	Same reactivity assumed as $\text{CH}_3\text{O}_2$
43	$\text{HOCH}_2\text{OO} + \text{OH} = \text{HOCH}_2\text{O} + \text{HO}_2$	$3.00\text{E}+12$	0	0	Same reactivity assumed as $\text{CH}_3\text{O}_2$
44	$\text{HOCH}_2\text{OO} + \text{HO}_2 = \text{HOCH}_2\text{OOH} + \text{O}_2$	$2.52\text{E}+11$	0	-1490	Same reactivity assumed as $\text{CH}_3\text{O}_2$
45	$\text{HOCH}_2\text{OO} + \text{HO}_2 = \text{CH}_2\text{OO} + \text{H}_2\text{O} + \text{O}_2$	$9.60\text{E}+08$	0	-3440	Same reactivity assumed as $\text{CH}_3\text{O}_2$
46	$\text{HOCH}_2\text{OO} + \text{H}_2\text{O}_2 = \text{HOCH}_2\text{OOH} + \text{HO}_2$	$2.40\text{E}+12$	0	9940	Same reactivity assumed as $\text{CH}_3\text{O}_2$
47	$\text{HOCH}_2\text{OO} + \text{B}_5\text{CH}_2 = \text{HCHO} + \text{HOCH}_2\text{O}$	$1.80\text{E}+13$	0	0	Same reactivity assumed as $\text{CH}_3\text{O}_2$
48	$\text{HOCH}_2\text{OO} + \text{CH}_3 = \text{CH}_3\text{O} + \text{HOCH}_2\text{O}$	$5.00\text{E}+12$	0	-1410	Same reactivity assumed as $\text{CH}_3\text{O}_2$
49	$\text{CH}_4 + \text{HOCH}_2\text{OO} = \text{CH}_3 + \text{HOCH}_2\text{OOH}$	$1.81\text{E}+11$	0	18480	Same reactivity assumed as $\text{CH}_3\text{O}_2$
50	$\text{HOCH}_2\text{OO} + \text{CO} = \text{HOCH}_2\text{O} + \text{CO}_2$	$1.00\text{E}+14$	0	24000	Same reactivity assumed as $\text{CH}_3\text{O}_2$
51	$\text{HCHO} + \text{HOCH}_2\text{OO} = \text{CHO} + \text{HOCH}_2\text{OOH}$	$2.00\text{E}+12$	0	11660	Same reactivity assumed as $\text{CH}_3\text{O}_2$
52	$\text{HOCH}_2\text{OO} + \text{CH}_3\text{O} = \text{HCHO} + \text{HOCH}_2\text{OOH}$	$3.00\text{E}+11$	0	0	Same reactivity assumed as $\text{CH}_3\text{O}_2$
53	$\text{CH}_3\text{OH} + \text{HOCH}_2\text{OO} = \text{CH}_2\text{OH} + \text{HOCH}_2\text{OOH}$	$1.81\text{E}+12$	0	13700	Same reactivity assumed as $\text{CH}_3\text{O}_2$
54	$\text{HOCH}_2\text{OO} + \text{CH}_3\text{OH} = \text{HOCH}_2\text{OOH} + \text{CH}_3\text{O}$	$2.80\text{E}+11$	0	18800	Same reactivity assumed as $\text{CH}_3\text{O}_2$
55	$\text{HOCH}_2\text{OOH} = \text{HOCH}_2\text{O} + \text{OH}$	$6.00\text{E}+14$	0	42300	Same reactivity assumed as $\text{CH}_3\text{O}_2\text{H}$ (Konnov 2000)
56	$\text{HOCH}_2\text{OOH} + \text{H} = \text{H}_2 + \text{HOCH}_2\text{OO}$	$8.79\text{E}+10$	0	1860	Same reactivity assumed as $\text{CH}_3\text{O}_2\text{H}$
57	$\text{HOCH}_2\text{OOH} + \text{H} = \text{H}_2\text{O} + \text{HOCH}_2\text{O}$	$7.27\text{E}+10$	0	1860	Same reactivity assumed as $\text{CH}_3\text{O}_2\text{H}$
58	$\text{HOCH}_2\text{OOH} + \text{O} = \text{OH} + \text{HOCH}_2\text{OO}$	$2.80\text{E}+13$	0	6400	Same reactivity assumed as $\text{CH}_3\text{O}_2\text{H}$
59	$\text{HOCH}_2\text{OOH} + \text{OH} = \text{HOCH}_2\text{OO} + \text{H}_2\text{O}$	$1.08\text{E}+12$	0	-437	Same reactivity assumed as $\text{CH}_3\text{O}_2\text{H}$
<b>C<sub>2</sub> species</b>					
60	$\text{C}_2\text{H}_2 + \text{OH} = \text{H} + \text{HCCOH}$	$5.06\text{E}+05$	2.3	13500	Miller and Melius, 1989
61	$\text{HCCOH} + \text{H} = \text{H} + \text{CH}_2\text{CO}$	$1.00\text{E}+13$	0	0	Thomson et al., 1994
62	$\text{HCCOH} + \text{O} = \text{CHCO} + \text{OH}$	$1.00\text{E}+10$	0	0	Estimate

63	C2H2+OH(+M)=C2H2OH(+M)	2.28E+13	0	1800	Atkinson et al., 1997
	LOW	9.34E+21	-1.5		
64	C2H2OH=CH2CO+H	5.00E+15	0	28000	Dagaut et al., 2000
65	C2H2OH+H=CH2CO+H2	2.00E+13	0	4000	Dagaut et al., 2000
66	C2H2OH+O=CH2CO+OH	2.00E+13	0	4000	Dagaut et al., 2000
67	C2H2OH+OH=CH2CO+H2O	1.00E+13	0	2000	Dagaut et al., 2000
68	C2H2OH+O2=CHOCHO+OH	1.00E+12	0	5000	Dagaut et al., 2000
69	C2H2OH+O2=CHO+CO2+H2	4.00E+12	0	-250	Dagaut et al., 2000
70	H2CCOH=CH2CO+H	5.00E+15	0	28000	Same reactivity assumed as C2H2OH (Konnov, 2000)
71	H2CCOH+H=CH2CO+H2	2.00E+13	0	4000	Same reactivity assumed as C2H2OH
72	H2CCOH+O=CH2CO+OH	2.00E+13	0	4000	Same reactivity assumed as C2H2OH
73	H2CCOH+OH=CH2CO+H2O	1.00E+13	0	2000	Same reactivity assumed as C2H2OH
74	H2CCOH+O2=CHOCHO+OH	1.00E+12	0	5000	Same reactivity assumed as C2H2OH
75	H2CCOH+O2=CHO+CO2+H2	4.00E+12	0	-250	Same reactivity assumed as C2H2OH
76	CH2CHOH+H=C2H2OH+H2	1.64E+07	2.0	10000	Same reactivity assumed as CH3OH (Konnov, 2000)
77	CH2CHOH+H=H2CCOH+H2	4.00E+13	0	10000	Same reactivity assumed as CH3OH
78	CH2CHOH+H=CH2CHO+H2	4.00E+13	0	10000	Same reactivity assumed as CH3OH
79	CH2CHOH+O=C2H2OH+OH	1.63E+13	0	12000	Same reactivity assumed as CH3OH
80	CH2CHOH+O=H2CCOH+OH	1.00E+13	0	10000	Same reactivity assumed as CH3OH
81	CH2CHOH+O=CH2CHO+OH	1.00E+13	0	5000	Same reactivity assumed as CH3OH
82	CH2CHOH+OH=H2CCOH+H2O	1.00E+13	0	1700	Same reactivity assumed as CH3OH
83	CH2CHOH+OH=C2H2OH+H2O	1.44E+06	2.0	-840	Same reactivity assumed as CH3OH
84	CH2CHOH+OH=CH2CHO+H2O	1.00E+13	0	1700	Same reactivity assumed as CH3OH
85	CH2CHOH+O2=H2CCOH+HO2	2.05E+13	0	64000	Same reactivity assumed as CH3OH
86	CH2CHOH+HO2=H2CCOH+H2O2	9.64E+10	0	25000	Same reactivity assumed as CH3OH
87	CH2CHOH+CH3=C2H2OH+CH4	3.19E+01	3.17	10000	Same reactivity assumed as CH3OH
88	CH2CHOH+CH3=H2CCOH+CH4	1.45E+01	3.1	10000	Same reactivity assumed as CH3OH
89	CH2CHOH+CH3=CH2CHO+CH4	1.45E+01	3.1	7000	Same reactivity assumed as CH3OH
90	CHOCO=CHO+CO	1.42E+12	0	6280	Orlando and Tyndall, 2001
91	CHOCO+O2=CO+CO+HO2	3.00E+12	0	0	Rate constant taken as that used by Konnov (2000) for HCO+O2=CO+HO2
92	CHO+CHO=CHOCHO	3.00E+13	0	0	Stoeckel et al., 1985
93	C2H3+O2=CHOCHO+H	1.47E+23	-3.83	6240	Thompson et al., 1994
94	CH2CHO+O2=CHOCHO+OH	2.76E+12	0	3000	Dagaut et al., 2000
95	CHOCHO=HCHO+CO	1.17E+16	-1.28	50937	Dagaut et al., 2000
96	CHOCHO=CO+CO+H2	6.52E+39	-7.70	67469	Dagaut et al., 2000

97	CHOCHO+H=HCHO+CHO	1.00E+12	0	0	Dagaut et al., 2000
98	CHOCHO+O=CHOCO+OH	7.24E+12	0	1970	Dagaut et al., 2000
99	CHOCHO+OH=CHOCO+H2O	6.60E+12	0	0	Atkinson et al., 1997
100	CHOCHO+O2=CHO+CO+HO2	6.30E+13	0	30000	Dagaut et al., 2000
101	CHOCHO+HO2=CHOCO+H2O2	1.70E+12	0	10700	Dagaut et al., 2000
102	CHOCHO+CH3=CHOCO+CH4	1.74E+12	0	8440	Dagaut et al., 2000
103	CH3CO2+M=CH3+CO2+M	8.70E+15	0	14400	Wilk et al. 1989
104	CH2OH+CO+M=HOCH2CO+M	1.00E+14	0	3000	Same reactivity assumed as CH3CO (Konnov, 2000)
105	HOCH2CO+H=CH2OH+CHO	2.15E+13	0	0	Same reactivity assumed as CH3CO
106	HOCH2CO+O=CH2OH+CO2	1.58E+14	0	0	Same reactivity assumed as CH3CO
107	HOCH2CO+OH=CH2OH+HOCO	3.00E+13	0	0	Same reactivity assumed as CH3CO
108	HOCH2CO+O2=HOCH2O+CO2	4.44E+10	0	-1080	Same reactivity assumed as CH3CO
109	HOCH2CO+HO2=CH2OH+CO2+OH	3.00E+13	0	0	Same reactivity assumed as CH3CO
110	HOCH2CO+CH3=C2H5OH+CO	3.30E+13	0	0	Same reactivity assumed as CH3CO
111	HOCH2CO+CHO=HOCH2CHO+CO	9.00E+12	0	0	Same reactivity assumed as CH3CO
112	HOCH2CO+HCHO=HOCH2CHO+CHO	1.80E+11	0	12900	Same reactivity assumed as CH3CO
113	HOCH2CO+CH3O=HCHO+HOCH2CHO	6.00E+12	0	0	Same reactivity assumed as CH3CO
114	HOCH2CO+CH3OH=HOCH2CHO+CH2OH	4.85E+03	3.0	12340	Same reactivity assumed as CH3CO
115	HOCHCHO=HOCH2CO	1.00E+13	0	47000	Same reactivity assumed as CH2CHO (Konnov, 2000)
116	HOCHCHO=CH2OH+CO	7.80E+41	-9.15	46900	Same reactivity assumed as CH2CHO
117	HOCHCHO+O=HCOOH+CHO	9.60E+06	1.83	220	Same reactivity assumed as CH2CHO
118	HOCHCHO+HO2=HCOOH+CHO+OH	1.10E+13	0	0	Same reactivity assumed as CH2CHO
119	HOCHCHO+CH3=SC2H5O+CHO	4.90E+14	-0.5	0	Same reactivity assumed as CH2CHO
120	CHCHOOH=CH2CO+OH	3.16E+11	0	19500	Same reactivity assumed as CH2CH2OOH (Konnov, 2000)
121	CHCHOOH=HOCHCHO	2.60E+12	0	20000	Same reactivity assumed as CH2CH2OOH
122	C2H3+O2=C2H3O2	6.00E+12	0	0	Same reactivity assumed as C2H5O2 (Konnov, 2000)
123	C2H3O2=CHCHOOH	2.00E+12	0	40000	Same reactivity assumed as C2H5O2
124	C2H3O2=C2H2+HO2	5.00E+11	0	40000	Same reactivity assumed as C2H5O2
125	C2H3O2+H2=C2H3OOH+H	3.00E+12	0	21000	Same reactivity assumed as C2H5O2
126	C2H3O2+HO2=C2H3OOH+O2	3.00E+11	0	-1000	Same reactivity assumed as C2H5O2
127	C2H3O2+HO2=CH2CHO+OH+O2	1.80E+12	0	0	Same reactivity assumed as C2H5O2
128	C2H3O2+H2O2=C2H3OOH+HO2	4.00E+11	0	11000	Same reactivity assumed as C2H5O2
129	C2H3O2+CH3=CH2CHO+CH3O	3.00E+13	0	0	Same reactivity assumed as C2H5O2

130	$\text{CH}_4 + \text{C}_2\text{H}_3\text{O}_2 = \text{CH}_3 + \text{C}_2\text{H}_3\text{OOH}$	$1.00\text{E}+13$	0	21000	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2$
131	$\text{HCHO} + \text{C}_2\text{H}_3\text{O}_2 = \text{CHO} + \text{C}_2\text{H}_3\text{OOH}$	$1.00\text{E}+11$	0	9000	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2$
132	$\text{C}_2\text{H}_3\text{O}_2 + \text{CH}_3\text{OH} = \text{C}_2\text{H}_3\text{OOH} + \text{CH}_3\text{O}$	$1.00\text{E}+11$	0	19000	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2$
133	$\text{CH}_3\text{OH} + \text{C}_2\text{H}_3\text{O}_2 = \text{CH}_2\text{OH} + \text{C}_2\text{H}_3\text{OOH}$	$6.00\text{E}+12$	0	20000	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2$
134	$\text{C}_2\text{H}_3\text{O}_2 + \text{CH}_3\text{OO} = \text{CH}_2\text{CHO} + \text{CH}_3\text{O} + \text{O}_2$	$1.00\text{E}+11$	0	0	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2$
135	$\text{C}_2\text{H}_3\text{O}_2 + \text{CH}_3\text{OOH} = \text{C}_2\text{H}_3\text{OOH} + \text{CH}_3\text{OO}$	$1.00\text{E}+12$	0	16000	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2$
136	$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_3\text{O}_2 = \text{C}_2\text{H}_3 + \text{C}_2\text{H}_3\text{OOH}$	$1.00\text{E}+13$	0	31000	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2$
137	$\text{C}_2\text{H}_3\text{O}_2 + \text{C}_2\text{H}_4 = \text{CH}_2\text{CHO} + \text{C}_2\text{H}_4\text{O}\#3$	$2.00\text{E}+12$	0	18000	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2$
138	$\text{C}_2\text{H}_3\text{O}_2 + \text{C}_2\text{H}_6 = \text{C}_2\text{H}_3\text{OOH} + \text{C}_2\text{H}_5$	$1.00\text{E}+13$	0	21000	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2$
139	$\text{C}_2\text{H}_3\text{O}_2 + \text{CH}_2\text{CO} = \text{C}_2\text{H}_3\text{OOH} + \text{CHCO}$	$1.00\text{E}+12$	0	25000	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2$
140	$\text{CH}_3\text{CHO} + \text{C}_2\text{H}_3\text{O}_2 = \text{CH}_3\text{CO} + \text{C}_2\text{H}_3\text{OOH}$	$1.00\text{E}+11$	0	10000	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2$
141	$\text{C}_2\text{H}_3\text{O}_2 + \text{CH}_3\text{CHO} = \text{C}_2\text{H}_3\text{OOH} + \text{CH}_2\text{CHO}$	$1.00\text{E}+12$	0	20000	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2$
142	$\text{C}_2\text{H}_3\text{O}_2 + \text{C}_2\text{H}_3\text{O}_2 = \text{CH}_2\text{CHO} + \text{CH}_2\text{CHO} + \text{O}_2$	$4.00\text{E}+10$	0	0	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2$
143	$\text{C}_2\text{H}_3\text{OOH} = \text{OH} + \text{CH}_2\text{CHO}$	$7.00\text{E}+14$	0	42000	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2\text{H}$ (Konnov, 2000)
144	$\text{C}_2\text{H}_3\text{OOH} + \text{O} = \text{OH} + \text{C}_2\text{H}_3\text{O}_2$	$2.80\text{E}+13$	0	6400	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2\text{H}$
145	$\text{C}_2\text{H}_3\text{OOH} + \text{O} = \text{OH} + \text{CHCHOOH}$	$6.00\text{E}+13$	0	10000	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2\text{H}$
146	$\text{C}_2\text{H}_3\text{OOH} + \text{OH} = \text{C}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O}$	$6.00\text{E}+11$	0	-380	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2\text{H}$
147	$\text{C}_2\text{H}_3\text{OOH} + \text{OH} = \text{CHCHOOH} + \text{H}_2\text{O}$	$6.00\text{E}+11$	0	-380	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2\text{H}$
148	$\text{C}_2\text{H}_3\text{OOH} + \text{C}_2\text{H} = \text{C}_2\text{H}_3\text{O}_2 + \text{C}_2\text{H}_2$	$6.00\text{E}+12$	0	0	Same reactivity assumed as $\text{C}_2\text{H}_5\text{O}_2\text{H}$
149	$\text{CH}_3\text{COOO} + \text{CH}_3\text{OO} = \text{CH}_3\text{CO}_2\text{H} + \text{HCHO} + \text{O}_2$	$2.47\text{E}+09$	0	-4200	Moortgat et al., 1989
150	$\text{CH}_3\text{CO} + \text{OH} = \text{CH}_3\text{CO}_2\text{H}$	$1.00\text{E}+14$	0	0	See present work
151	$\text{CH}_3\text{CO}_2\text{H} = \text{CH}_4 + \text{CO}_2$	$7.08\text{E}+13$	0	74600	Duan and Page, 1995
152	$\text{CH}_3\text{CO}_2\text{H} = \text{CH}_2\text{CO} + \text{H}_2\text{O}$	$4.47\text{E}+14$	0	79800	Duan and Page, 1995
153	$\text{CH}_3\text{CO}_2\text{H} + \text{OH} = \text{CH}_3\text{CO}_2 + \text{H}_2\text{O}$	$2.40\text{E}+11$	0	-400	DeMore et al., 1997
154	$\text{CH}_2\text{OH} + \text{CHO} = \text{HOCH}_2\text{CHO}$	$1.80\text{E}+13$	0	0	Estimate
155	$\text{HOCH}_2\text{CHO} + \text{OH} = \text{HOCH}_2\text{CO} + \text{H}_2\text{O}$	$6.00\text{E}+12$	0	0	Atkinson et al., 2005
156	$\text{HOCH}_2\text{CHO} + \text{OH} = \text{HOCHCHO} + \text{H}_2\text{O}$	$1.50\text{E}+12$	0	0	Atkinson et al., 2005
157	$\text{C}_2\text{H}_5 + \text{O}_2 = \text{C}_2\text{H}_4\text{OOH}$	$1.02\text{E}+50$	-12.4	15460	Thompson et al., 1994
158	$\text{C}_2\text{H}_5\text{OOH} + \text{O} = \text{OH} + \text{C}_2\text{H}_4\text{OOH}$	$3.55\text{E}+06$	2.4	5830	Same rate constant as $\text{C}_2\text{H}_6 + \text{O}$ (Konnov, 2000)
159	$\text{C}_2\text{H}_5\text{OOH} + \text{OH} = \text{C}_2\text{H}_4\text{OOH} + \text{H}_2\text{O}$	$6.00\text{E}+11$	0	-380	Baulch et al., 2005
160	$\text{C}_2\text{H}_5\text{OOH} + \text{O} = \text{OH} + \text{CH}_3\text{CHOOH}$	$6.60\text{E}+13$	0	4150	Baulch et al., 2005 (total rate attributed to this channel)
161	$\text{C}_2\text{H}_5\text{OOH} + \text{OH} = \text{CH}_3\text{CHOOH} + \text{H}_2\text{O}$	$6.00\text{E}+11$	0	-380	Same reactivity assumed as $\text{C}_2\text{H}_4\text{OOH}$
162	$\text{CH}_3\text{CHOOH} = \text{CH}_3\text{CHO} + \text{OH}$	$3.16\text{E}+11$	0	19500	Estimate
163	$\text{CH}_3\text{CHOOH} = \text{C}_2\text{H}_4\text{O}\#3 + \text{OH}$	$3.16\text{E}+11$	0	19500	Estimate

<b>C<sub>3</sub> species</b>					
164	CHO+C <sub>2</sub> H <sub>5</sub> =>C <sub>2</sub> H <sub>5</sub> CHO	1.80E+13	0	0	Tsang and Hampson, 1986
165	C <sub>2</sub> H <sub>5</sub> CHO+H=H <sub>2</sub> +C <sub>2</sub> H <sub>5</sub> CO	4.00E+13	0	4200	Same reactivity assumed as CH <sub>3</sub> CHO
166	C <sub>2</sub> H <sub>5</sub> CHO+CH <sub>3</sub> =C <sub>2</sub> H <sub>5</sub> CO+CH <sub>4</sub>	2.00E-06	5.6	2500	(Barbé et al., 1995) Same reactivity assumed as CH <sub>3</sub> CHO
167	C <sub>2</sub> H <sub>5</sub> CHO+C <sub>2</sub> H <sub>3</sub> =C <sub>2</sub> H <sub>4</sub> +C <sub>2</sub> H <sub>5</sub> CO	8.10E+10	0	3700	Same reactivity assumed as CH <sub>3</sub> CHO
168	C <sub>2</sub> H <sub>5</sub> CHO+C <sub>2</sub> H <sub>5</sub> =C <sub>2</sub> H <sub>6</sub> +C <sub>2</sub> H <sub>5</sub> CO	1.30E+12	0	8500	Same reactivity assumed as CH <sub>3</sub> CHO
169	C <sub>2</sub> H <sub>5</sub> CHO+O=C <sub>2</sub> H <sub>5</sub> CO+OH	1.40E+13	0	2300	Same reactivity assumed as CH <sub>3</sub> CHO
170	C <sub>2</sub> H <sub>5</sub> CHO+OH=C <sub>2</sub> H <sub>5</sub> CO+H <sub>2</sub> O	4.20E+12	0	500	Same reactivity assumed as CH <sub>3</sub> CHO
171	C <sub>2</sub> H <sub>5</sub> CHO+CH <sub>3</sub> O=C <sub>2</sub> H <sub>5</sub> CO+CH <sub>3</sub> OH	2.40E+11	0	1800	Same reactivity assumed as CH <sub>3</sub> CHO
172	CH <sub>2</sub> CO+CH <sub>3</sub> =C <sub>2</sub> H <sub>5</sub> CO	2.40E+12	0	8000	Borisov et al., 1990 Formation of C <sub>2</sub> H <sub>5</sub> CO assumed instead of that of C <sub>2</sub> H <sub>5</sub> +CO
173	C <sub>2</sub> H <sub>5</sub> CO+OH=C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H	1.00E+14	0	0	See present work
174	C <sub>2</sub> H <sub>5</sub> CO=C <sub>2</sub> H <sub>5</sub> +CO	5.89E+12	0	14400	Watkins and Thompson, 1973
175	C <sub>2</sub> H <sub>5</sub> CO+H=C <sub>2</sub> H <sub>5</sub> +CHO	9.60E+13	0	0	Same reactivity assumed as CH <sub>3</sub> CO
176	C <sub>2</sub> H <sub>5</sub> CO+B <sub>6</sub> CH <sub>2</sub> =C <sub>2</sub> H <sub>5</sub> +CH <sub>2</sub> CO	1.80E+13	0	0	(Barbé et al., 1995) Same reactivity assumed as CH <sub>3</sub> CO
177	C <sub>2</sub> H <sub>5</sub> CO+B <sub>5</sub> CH <sub>2</sub> =C <sub>2</sub> H <sub>5</sub> +CH <sub>2</sub> CO	1.80E+13	0	0	Same reactivity assumed as CH <sub>3</sub> CO
178	C <sub>2</sub> H <sub>5</sub> CO+O=C <sub>2</sub> H <sub>5</sub> +CO <sub>2</sub>	9.60E+12	0	0	Same reactivity assumed as CH <sub>3</sub> CO
179	C <sub>2</sub> H <sub>5</sub> CO+OH=>C <sub>2</sub> H <sub>5</sub> +CO+OH	3.00E+13	0	0	Same reactivity assumed as CH <sub>3</sub> CO
180	C <sub>2</sub> H <sub>5</sub> CO+CHO=C <sub>2</sub> H <sub>5</sub> CHO+CO	9.00E+12	0	0	Same reactivity assumed as CH <sub>3</sub> CO
181	C <sub>2</sub> H <sub>5</sub> CO+HCHO=C <sub>2</sub> H <sub>5</sub> CHO+CHO	1.80E+11	0	12900	Same reactivity assumed as CH <sub>3</sub> CO
182	C <sub>2</sub> H <sub>5</sub> CO+CH <sub>3</sub> O=HCHO+C <sub>2</sub> H <sub>5</sub> CHO	6.00E+12	0	0	Same reactivity assumed as CH <sub>3</sub> CO
183	C <sub>2</sub> H <sub>5</sub> CO+CH <sub>3</sub> OH=C <sub>2</sub> H <sub>5</sub> CHO+CH <sub>2</sub> OH	4.85E+03	3.0	12300	Same reactivity assumed as CH <sub>3</sub> CO
184	O <sub>2</sub> +C <sub>2</sub> H <sub>5</sub> CO=C <sub>2</sub> H <sub>5</sub> COOO	2.40E+12	0	0	Same reactivity assumed as CH <sub>3</sub> CO
185	C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H=C <sub>2</sub> H <sub>6</sub> +CO <sub>2</sub>	7.08E+13	0	74600	See present work
186	C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H+OH=C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> +H <sub>2</sub> O	2.40E+11	0	-400	See present work
187	C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> +M=C <sub>2</sub> H <sub>5</sub> +CO <sub>2</sub> +M	8.70E+15	0	14400	See present work
188	C <sub>2</sub> H <sub>5</sub> COOO+CH <sub>3</sub> OO=C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H+HCHO+O <sub>2</sub>	2.47E+09	0	-4200	Same reactivity assumed as CH <sub>3</sub> COOO
189	C <sub>2</sub> H <sub>5</sub> COOO+C <sub>2</sub> H <sub>4</sub> O#3=C <sub>2</sub> H <sub>5</sub> COOOH+CH <sub>2</sub> CHO	1.00E+12	0	9300	(Barbé et al., 1995) Same reactivity assumed as CH <sub>3</sub> COOO
190	C <sub>2</sub> H <sub>5</sub> COOO+HO <sub>2</sub> =C <sub>2</sub> H <sub>5</sub> COOOH+O <sub>2</sub>	5.50E+10	0	-2600	Same reactivity assumed as CH <sub>3</sub> COOO
191	C <sub>2</sub> H <sub>5</sub> COOO+C <sub>2</sub> H <sub>5</sub> OOH=C <sub>2</sub> H <sub>5</sub> COOOH+C <sub>2</sub> H <sub>5</sub> OO	5.00E+11	0	9200	Same reactivity assumed as CH <sub>3</sub> COOO
192	C <sub>2</sub> H <sub>5</sub> COOO+C <sub>2</sub> H <sub>5</sub> COOO=>2C <sub>2</sub> H <sub>5</sub> +O <sub>2</sub> +2CO <sub>2</sub>	1.70E+12	0	-1000	Same reactivity assumed as CH <sub>3</sub> COOO
193	C <sub>2</sub> H <sub>5</sub> COOOH=>C <sub>2</sub> H <sub>5</sub> +CO <sub>2</sub> +OH	1.00E+16	0	40000	Same reactivity assumed as CH <sub>3</sub> COOO



194	$\text{CH}_2\text{CHCO} + \text{OH} = \text{C}_2\text{H}_3\text{CO}_2\text{H}$	1.00E+14	0	0	See present work
195	$\text{C}_2\text{H}_3\text{CO}_2\text{H} = \text{C}_2\text{H}_4 + \text{CO}_2$	7.08E+13	0	74600	See present work
196	$\text{C}_2\text{H}_3\text{CO}_2\text{H} + \text{OH} = \text{C}_2\text{H}_3\text{CO}_2 + \text{H}_2\text{O}$	2.40E+11	0	-400	See present work
197	$\text{C}_2\text{H}_3\text{CO}_2 + \text{M} = \text{C}_2\text{H}_3 + \text{CO}_2 + \text{M}$	8.70E+15	0	14400	See present work

### Figures captions:

- Figure 1: Modeling of a laminar premixed flame of propane at 1 atm for an equivalence ratio of 0.9. Symbols correspond to experiments of Biet et al. (2005) and lines to simulations.
- Figure 2: Modeling of a laminar premixed flame of propane at 1 atm for an equivalence ratio of 0.48. Symbols correspond to experiments of Biet et al. (2005) and lines to simulations.
- Figure 3: Modeling of the formation of acids in laminar premixed flames of propane at 1 atm for an equivalence ratio of (a) 0.9 and (b) 0.48.
- Figure 4: Comparison between experimental (Zervas (2005)) and simulated proportions of acids for an equivalence ratio of 0.9 at the maximum of the peak of formic acid.
- Figure 5: Main pathways of formation of the four monocarboxylic acids studied under the conditions of figure 3a for a distance above the burner corresponding to the maximum of the peak of formic acid (0.5 cm). The size of the arrows is proportional to the relative flow rates.
- Figure 6: Simulated profiles of the main aromatic species under the conditions of the flame of propane of Biet et al. (2005) at  $\phi=0.9$ , but with an addition of 10% toluene (relative to the mole fraction of propane).
- Figure 7: Formation of acids under the conditions of the flame of propane of Biet et al. (2005) at  $\phi=0.9$ , but with an addition of 10% toluene (relative to the mole fraction of propane).
- Figure 8: Simulated evolution of (a) the main  $C_1$ - $C_3$ , (b)  $C_7$  and  $C_8$  oxygenated species during the pre-ignition phase in an HCCI engine.
- Figure 9: Comparison of the mole fractions of acetaldehyde, acrolein, propionaldehyde and methanol relative to that of formaldehyde computed in this study and measured by Zervas et al. (2002).

Figure 10: Formation of  $C_1$ - $C_3$  acids and formaldehyde according to the different proposed models during the pre-ignition phase in an HCCI engine.

Figure 1

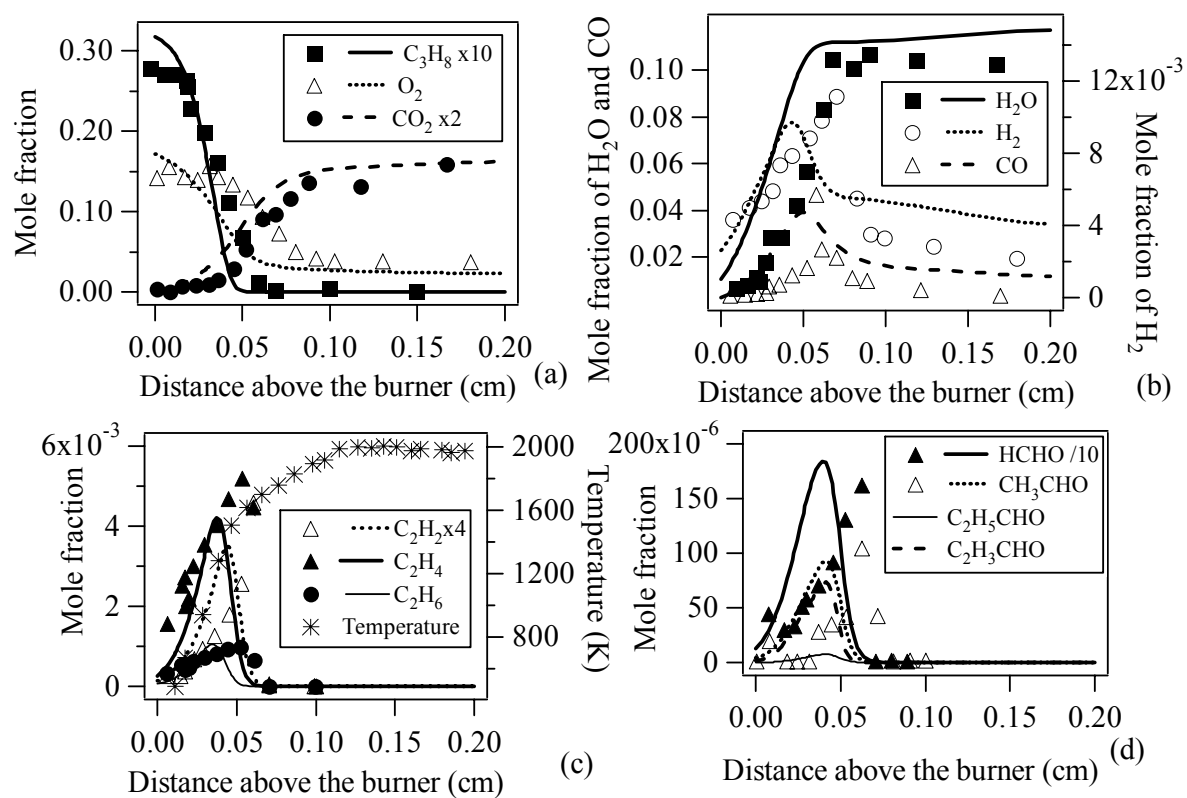


Figure 2

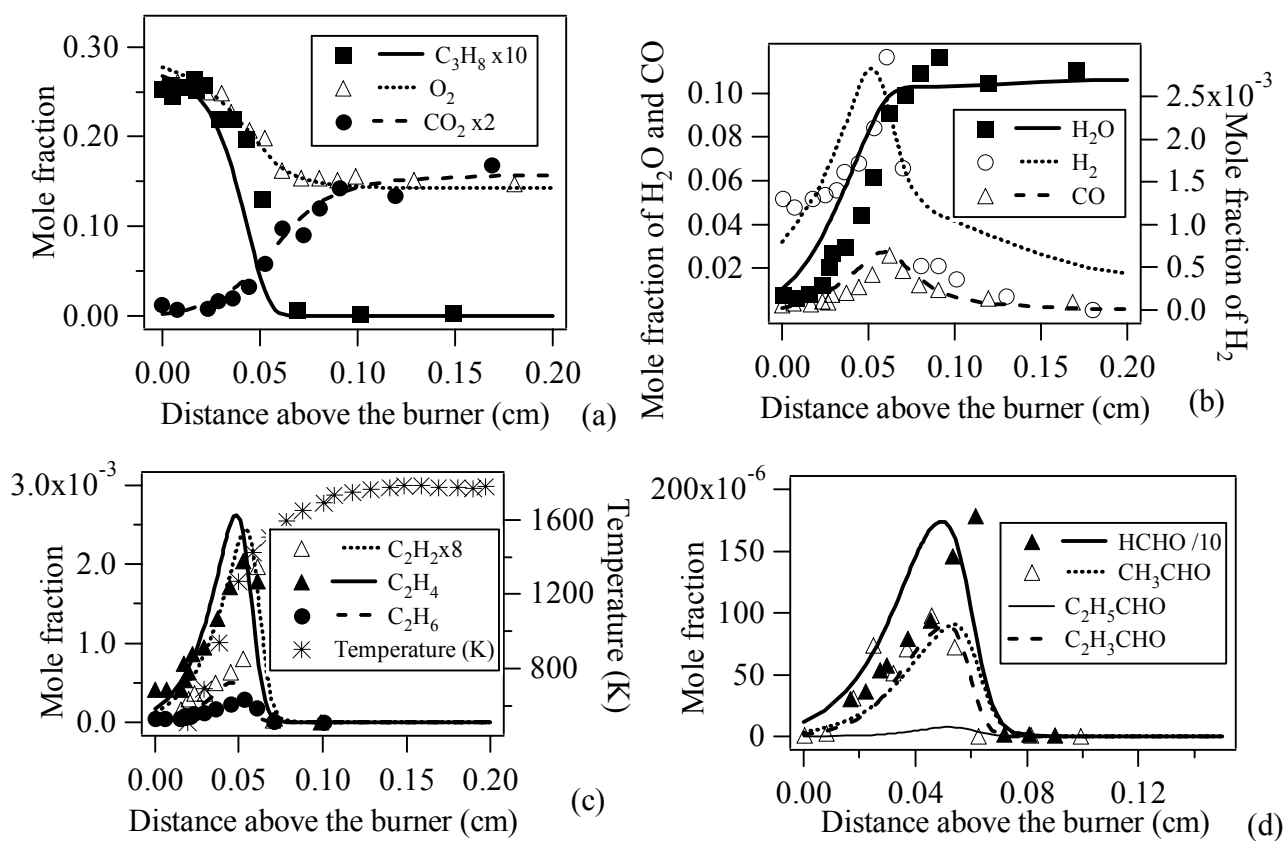


Figure 3

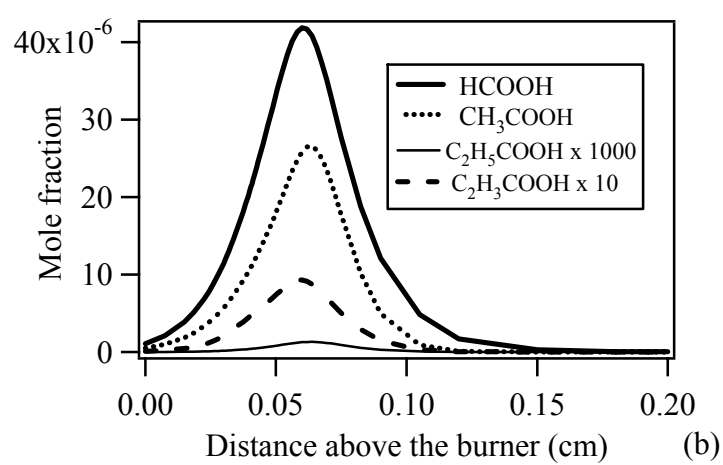
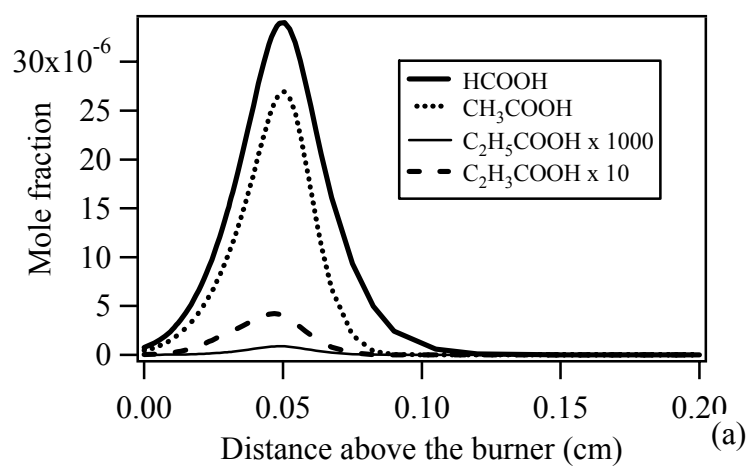


Figure 4

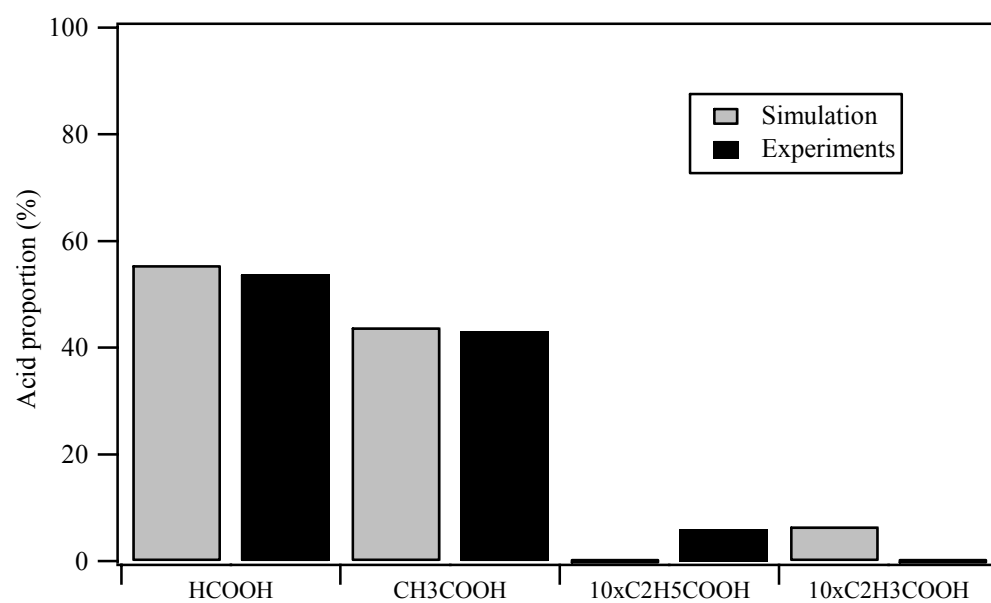


Figure 5

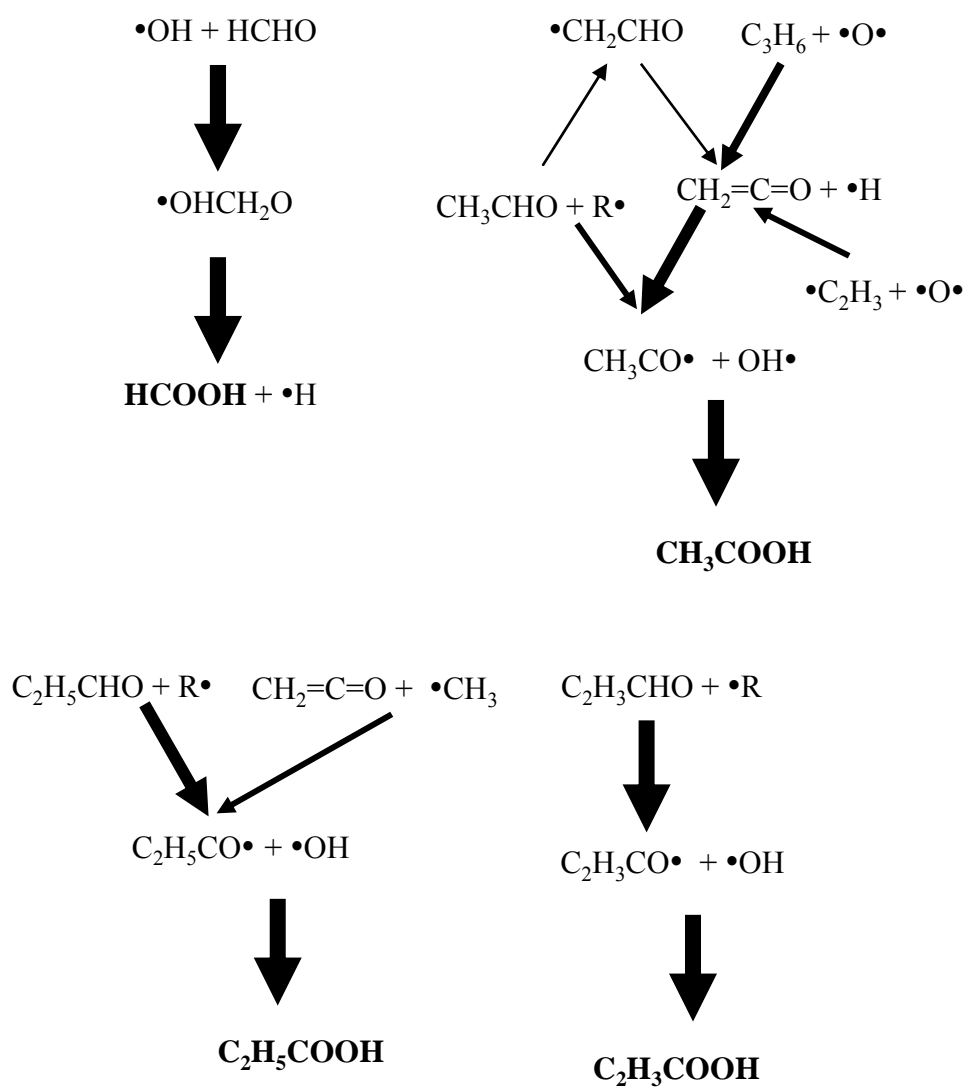




Figure 6

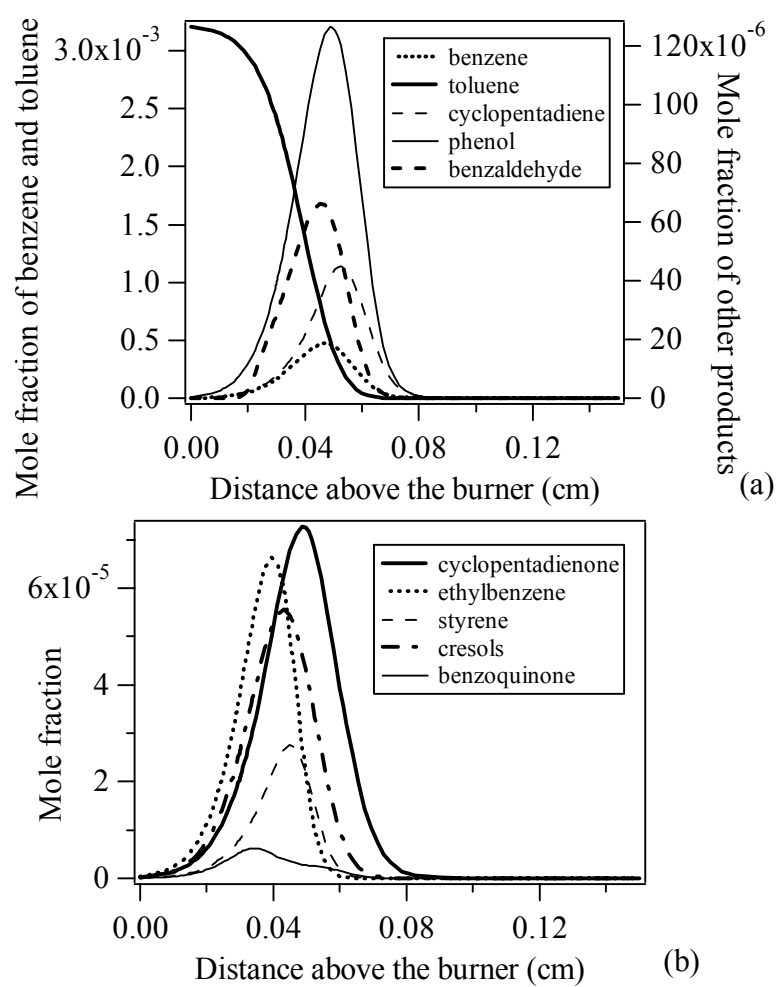


Figure 7

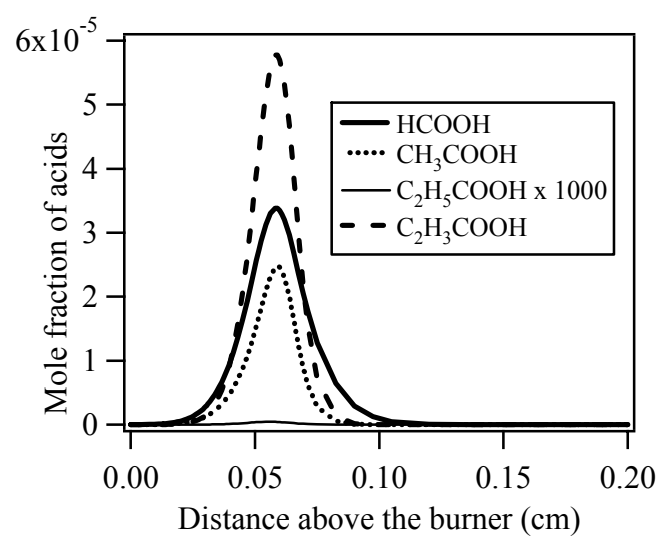


Figure 8

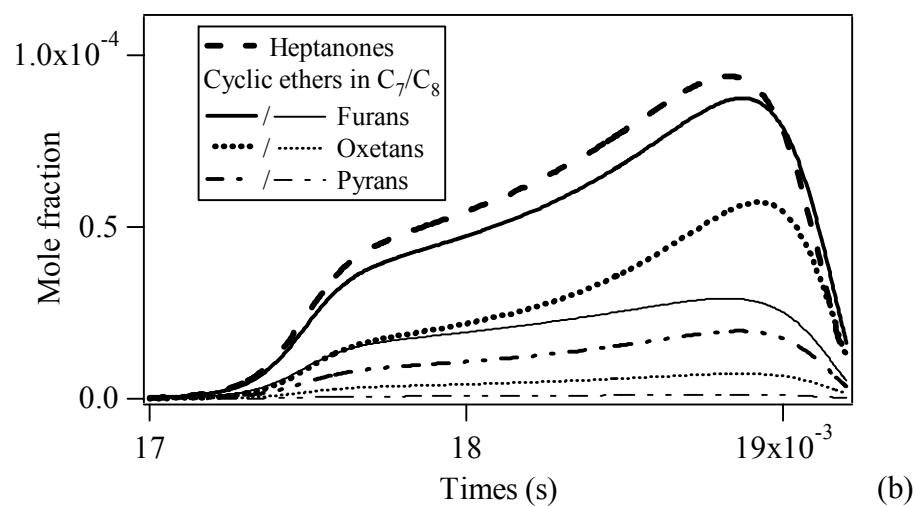
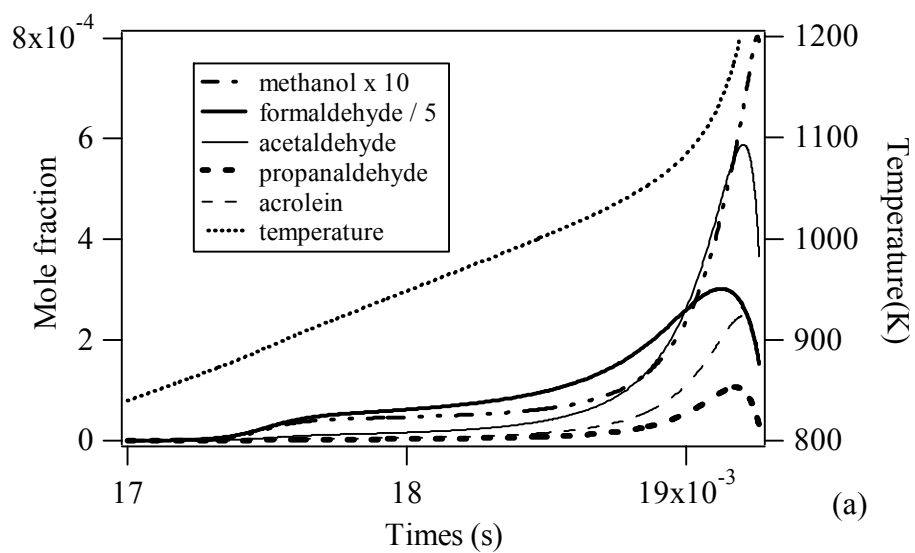


Figure 9

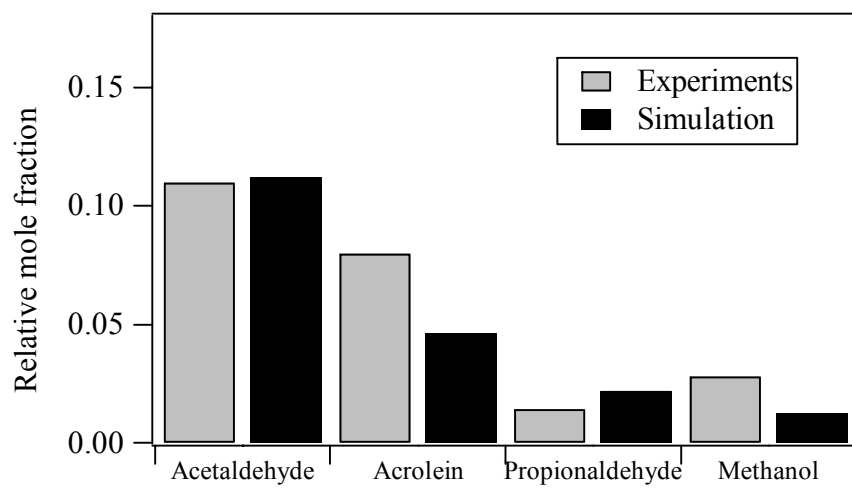


Figure 10

